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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

P1999S004

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/069321

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.  
PCT/EP00/07910

INTERNATIONAL FILING DATE  
11.08.00

PRIORITY DATE CLAIMED  
17.08.99

TITLE OF INVENTION

CRYSTAL FORMATION INHIBITION IN LUBRICATING COMPOSITIONS

APPLICANT(S) FOR DO/EO/US

David Gary Lawton Holt

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is the **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is the **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
  4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
    - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
    - b. ☐ has been communicated by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a. ☒ is attached hereto.
    - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
  7. ☒ Amendments to the claims of the International Application number PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
    - b. ☐ have been communicated by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☒ have not been made and will not be made.
  8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
  10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11 to 20 below concern document(s) or information included:**
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☐ A **FIRST** preliminary amendment.
  14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  15. ☐ A substitute specification.
  16. ☐ A change of power of attorney and/or address letter.
  17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
  18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
  19. ☐ A second copy of the English translation of the international application under 35 U.S.C. 154(d)(4).
  20. ☒ Other items or information:

PCT Request; International Application Number & International Filing Date; Receipt of Record Copy; The Recording of A Change; International Search Report; International Application to the Designated Offices; International Application as Published; International Preliminary Examination Report

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold; text-align: center;">10/069321</div>	INTERNATIONAL APPLICATION NO. PCT/EP00/07910	ATTORNEY'S DOCKET NUMBER P1999S004
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21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. .... \$1040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$750.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 <div style="text-align: center; font-weight: bold;">ENTER APPROPRIATE BASE FEE AMOUNT =</div> Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(c)). <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> <th style="width: 20%;">\$</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>16- 20 =</td> <td>0</td> <td>x \$18.00</td> <td>\$0.00</td> </tr> <tr> <td>Independent claims</td> <td>2- 3 =</td> <td>0</td> <td>x \$84.00</td> <td>\$0.00</td> </tr> <tr> <td colspan="3">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td>+ \$280.00</td> <td>\$280.00</td> </tr> <tr> <td colspan="4" style="text-align: center;"><b>TOTAL OF ABOVE CALCULATIONS =</b></td> <td>\$1,300.00</td> </tr> </tbody> </table> <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. <span style="float: right;">+</span> <div style="text-align: right; font-weight: bold;">SUBTOTAL =</div> \$1,300.00 Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). <div style="text-align: right; font-weight: bold;">TOTAL NATIONAL FEE =</div> \$1,300.00 Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property <span style="float: right;">+</span> <div style="text-align: right; font-weight: bold;">TOTAL FEES ENCLOSED =</div> \$1,300.00 <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%;">Amount to be refunded:</td> <td style="width: 20%;">\$</td> </tr> <tr> <td>charged:</td> <td>\$</td> </tr> </table>	CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	Total claims	16- 20 =	0	x \$18.00	\$0.00	Independent claims	2- 3 =	0	x \$84.00	\$0.00	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$280.00	<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$1,300.00	Amount to be refunded:	\$	charged:	\$	CALCULATIONS PTO USE ONLY
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a. ☐ A check in the amount of \$\_\_\_\_\_ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 95-1330 in the amount of \$1300.00 to cover the above fees.  
 A duplicate copy of this sheet is enclosed.

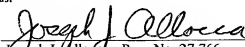
c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment  
 to Deposit Account No. 95-1330. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card  
 information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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10069321 10/069321  
J Rec'd PCT/PTO 19 FEB 2002

PCT INTERNATIONAL APPLICATION TRANSMITTAL LETTER	DATE February 19, 2002
REGARDING THE INTERNATIONAL APPLICATION OF EXXONMOBIL RESEARCH AND ENGINEERING COMPANY	DOCKET OR REFERENCE NUMBER P1999S004
Entitled CRYSTAL FORMATION INHIBITION IN LUBRICATING COMPOSITIONS	

**Certification under 37 CFR 1.10 (if applicable)**

EJ083185424US

"Express Mail" mailing number

February 19, 2002

Date of Deposit

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Teresa L. Lachowski

(Typed or printed name of person mailing application)

*Teresa L. Lachowski*  
(Signature of person mailing application)

To the United States Receiving Office (RO/US):

Accompanying this transmittal letter is the above-identified International application, including a completed Request form (PCT/RO/101). Please process the application according to the provisions of the Patent Cooperation Treaty.



27810

PATENT TRADEMARK OFFICE

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## STABILIZED LUBRICATING FORMULATION AND METHOD

This invention relates to lubricating oil based on base stocks having  
10 less than 99 wt% saturates content and containing one or more sulfur-  
phosphorus containing anti-wear/extreme pressure additives and one or more  
hindered phenol anti oxidants which combination are prone to crystal formation,  
wherein the formation of crystals is reduced or eliminated by the use of a  
crystallization suppressant.

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Lubricating oils containing various antioxidants or esters or fatty acid amides or sulfur-phosphorus additives in combination with phenols are known in the literature.

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U.S. Patent 5,167,844 is directed to a formulation comprising a base oil, at least one sulfur phosphorus containing compound, at least one amine and at least one hindered phenol.

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JP 07034078 is directed to a hydraulic oil comprising mineral oil with an aromatic content of up to 1.5 wt% and a phenolic and aminic anti-oxidant, an alkenyl succinic acid imide rust inhibitor and a phosphoric acid type anti wear agent.

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U.S. Patent 5,580,483 is directed for lubricating a refrigeration system compressor using a break-in lubricating oil which is an ester type oil. Additionally an adipate, phthalate, azelate, sebacate, trimellitate can also be present as well as tri hydrocarbyl phosphate, corrosion inhibitors such as alkali and/or alkaline earth metal sulfonate, antioxidants such as aminic or phenolic antioxidants and metal deactivators such as triazoles.

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WO 97/14776 is directed to hydraulic oils comprising base oils combined with an amine antioxidant, a phenolic antioxidant, a phosphate ester and a fatty acid amide and/or polyhydric alcohol ester.

10

U.S. Patent 5,773,393 is directed to a composition comprising at least 70 wt% oil of lubricating viscosity and an amount effective to inhibit metal corrosion of a soluble additive comprising (a) at least one amide compound of a mono- or polycarboxylic acid or reactive derivative thereof and (b) at least 0.5 equivalents of at least one primary or secondary amine per mole of amide provided that when (a) is an amide of a dicarboxylic acid and the amine is an alkanol amine the mixture contains more than 0.5 equivalent of the amine (b) per equivalent of the amide.

15

The present invention is directed to a lubricating oil formulation having a reduced potential for the formation of crystals comprising a major amount of a lubricating oil base stock having less than about 99 wt% saturates content, preferably less than about 98 wt% saturates content, and a minor amount of additives comprising a mixture of sulfur-phosphorus containing anti-wear/extreme pressure additive, hindered phenol antioxidant and one or more high molecular weight di-, or polycarboxylic acid, anhydride or mixture thereof such as polyolefin succinic acid/anhydride, and to a method for reducing crystal formation in lubricating oil formulations comprising base oil having less than about 99 wt% saturates content, preferably less than about 98 wt% saturates content, and containing sulfur phosphorus anti-wear/extreme pressure additive and hindered phenolic anti-oxidant wherein the crystals are attributed to the interaction between the sulfur phosphorus containing anti-wear/extreme pressure agent and the hindered phenol by adding to said lubricating oil a minor effective amount of one or more high molecular weight di- or polycarboxylic acid or

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- 5 anhydride such as polyolefin succinic acid/poly olefin succinic anhydride and/or mixtures thereof.

The lubricating base oil is any oil of lubricating oil viscosity having less than about 99 wt% saturates content, preferably less than about 98 wt%  
10 saturates content.

Lubricating oils meeting this criterion are any natural mineral or petroleum based lubricating oils derived from crude oil, tar sands, shale oil, etc., such that they contain a quantity of unsaturation resulting in a saturates content  
15 of less than of 99%, or a mixture of natural mineral or petroleum based lubricating oils in combination with a base oil or oils having a saturates content of greater than 99 wt%, e.g. hydrocarbon oils such as white oils and/or severely hydrotreated, hydrocracked mineral oils, or synthetic oils such as poly alpha olefins, esters, isomerized wax or isomerized Fischer-Tropsch wax, the  
20 combination or mixture of such oils being characterized as having less than about 99 wt% saturates. Saturates content, for the purposes of this specification, is a measure of the absence of aromatic species, and was determined by high pressure liquid chromatography (HPLC) according to method IP 368, except where otherwise expressly indicated.

25

The lubricating oil base stocks useful in the present invention have the typical lubricating oil viscosity, usually possessing kinematic viscosities in the range of about 1.5 to 500 mm<sup>2</sup>/s at 100°C, preferably 5 to 120 mm<sup>2</sup>/s at 100°C.

30

Mineral or petroleum based lubricating oil base stocks can be derived from paraffinic, naphthenic and mixed base crudes. Conventional refinery techniques include distillation, solvent and/or catalytic dewaxing,

- 5 solvent extraction, hydrofinishing, hydrocracking, vis breaking, deasphalting, etc.

Synthetic lubricating oils that can be used include esters of di- and tri-basic acids, reacted with linear or branched aliphatic alcohols such as C<sub>6</sub>-C<sub>15</sub> 10 alcohols, such as di-2-ethylhexyl sebacate, phthalic ester esters of glycols such as C<sub>13</sub> oxo acid diester or tetraethylene glycol, or complex esters such as one formed from 1 mole of sebacic acid and 2 moles of tetraethylene glycol and 2 moles of 2-ethylhexanoic acid. Other synthetic oils that can be used include synthetic hydrocarbons such as alkyl benzenes, e.g., alkylate bottoms from the 15 alkylation of benzene with tetrapropylene, or the copolymers of ethylene and propylene; silicone oils, e.g., ethyl phenyl polysiloxanes, methyl polysiloxanes, etc.; polyglycol oils, e.g., those obtained by condensing butyl alcohol with propylene oxide; carbonate esters, e.g., the product of reacting C<sub>6</sub> oxo alcohol with ethyl carbonate to form a half ester followed by reaction of the latter with 20 tetraethylene glycol, etc. Other suitable synthetic oils include the polyphenyl ethers, e.g., those having from about 3 to 7 ether linkages and about 4 to 8 phenyl groups.

Other suitable oils are the polyol ester oils made by reacting an 25 aliphatic polyol with carboxylic acid. Aliphatic polyols contain from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Examples of polyols are trimethylolpropane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol and mixtures thereof. The carboxylic acid reactant is selected from aliphatic monocarboxylic acid or mixtures of aliphatic mono 30 carboxylic acids or mixtures of aliphatic mono- and di-carboxylic acids. The carboxylic acids contain 4 to 12 carbons and include straight and branched chain carboxylic acids.

5 Included in the group of synthetic oils are those recovered from tar  
sands, shale oil, light hydrocarbons produced via, for example, the Fischer-  
Tropsch process for converting synthesis gas (CO and hydrogen) into hydro-  
carbons, wax isomerate oils produced by the catalytic hydroisomerization of  
10 natural petroleum waxes (i.e., slack wax) or synthetic waxes (i.e., Fischer-  
Tropsch waxes) or mixtures of such waxes. See USP 5,059,299 and USP  
5,158,671 for description of wax isomerization and the oils produced thereby.  
Other synthetic oils include the polyolefins such as polybutene, polyisobutenes  
and especially the polyalphaolefins, i.e., fluids formed by the oligomerization of  
at least one 1-alkane hydrocarbon having from 6 to 20 carbons, preferable 8 to  
15 16 carbons, more preferably 8 to 12 carbons.

Regardless of the source of the oil, for the purposes of the present  
invention, the lube oil base stock, be it a single oil or a mixture of oils, is  
characterized as having a saturates content of less than about 99%, preferably  
20 less than 98 wt%.

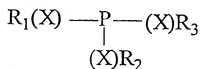
Sulfur-phosphorus containing anti-wear/extreme pressure additives  
are well known in the industry, and are materials containing both sulfur and  
phosphorus in the same molecule. For the purpose of the present specification,  
25 and appended claims sulfur-phosphorus containing anti wear, extreme pressure  
additives are those which react with hindered phenols to produce crystals. Those  
skilled in the formulation art can readily determine without expenditure of  
inventive effort, whether a particular sulfur-phosphorus containing anti-  
wear/extreme pressure agent reacts with hindered phenol anti-oxidant to produce  
30 crystals. If it does not, it is not within the scope of this invention. Any sulfur-  
phosphorus containing anti-wear/extreme pressure agent which is found to react  
with hindered phenol antioxidant to produce crystals in the subject base oil is  
within this invention and formalities containing such agents and phenolic



- 5 antioxidants will be beneficially affected is evidenced by reduction on  
elimination of crystal formation by the addition of the high molecular weigh di-  
or poly carboxylic acid, anhydride or mixture thereof, as shown below, provided  
such carboxylic acid, anhydride or mixture thereof is used in an amount of at  
least about 0.0013 wt% for each 1 ppm phosphorus attributable to the sulfur-  
10 phosphorus containing anti-wear/extreme pressure agent.

Sulfur-phosphorus anti-wear/extreme pressure additives which  
interact with hindered phenols to produce crystals are exemplified by, but not  
limited to, materials of the type:

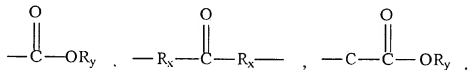
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wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently hydrogen or hydrocarbyl provided at  
least one is hydrocarbyl so as to render the material oil soluble and X is sulfur.

20

- The hydrocarbyl groups preferably contain from 1 to 40 carbons and  
are aromatic and/or aliphatic groups and include aryl alkyl and alkaryl and  
aralkyl and heteroatom substituted aromatic and aliphatic group, the heteroatom  
substitutents being sulfur, nitrogen or oxygen substituted as such into the  
25 hydrocarbon skeleton or as sulfur, oxygen or nitrogen containing moiety, e.g.,  
—OR<sub>y</sub>, —SH, —SO<sub>2</sub>H, —N(R<sub>y</sub>)<sub>2</sub>, —C—R<sub>x</sub>OR<sub>y</sub>,

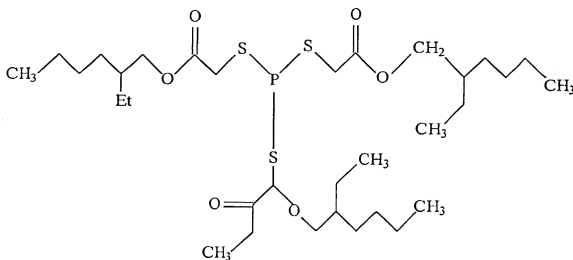


- 7 -

- 5 etc., and mixtures thereof substituted onto or into the hydrocarbon backbone, wherein  $R_x$  is  $C_1$ - $C_{20}$  hydrocarbyl or hydrocarbylene group and  $R_y$  is hydrogen or a  $C_1$ - $C_{20}$  hydrocarbyl or hydrocarbylene.

- Such sulfur-organo phosphorus containing anti-wear/extreme  
 10 pressure agent is typically used at a concentration sufficient to provide of from about 2 ppm to 320 ppm phosphorus, preferably 40 ppm to 200 ppm phosphorus, most preferably about 80 ppm to 130 ppm phosphorus.

- An example of a sulfur phosphorus anti-wear/extreme pressure  
 15 additive which has been found to react with hindered phenols to form crystals is a material is 2-ethylhexyl 10-ethyl-4-[[2-[(2 ethylhexyl)-oxyl]-2-oxoethyl] thio]-7-oxo-8-oxa-3,5-dithia-4-phospha tetradecanoate, CAS # 83547-95-9. Based on the name and the CAS number, it is believed this material has the following structure:

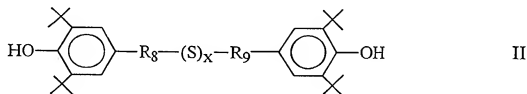


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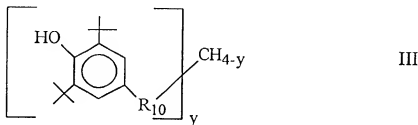
It must be noted that for the purposes of the present invention metal dihydrocarbyldithiophosphate (metal DDP) or ashless DDP do not fall within the above definition of sulfur-phosphorus containing anti-wear/extreme pressure

- 5 additive because it has been found that they do not form crystals when combined with hindered phenols in base oils.

Hindered phenolic anti oxidants are also well known in the industry. Such materials include by way of example and not limitation 2,6-di-t-butyl phenol, 2,6-di-t-butyl alkylated phenol where the alkyl substituent is hydrocarbyl  
 10 and contains between 1 and 20 carbon atoms, such as 2,6-di-t-butyl-4-methyl phenol, 2,6-di-t-butyl-4-ethyl phenol, etc., or 2,6-di-t-butyl-4-alkoxy phenol where the alkoxy substituent contains between 1 and 20 carbons such as 2,6-di-t-butyl-4-methoxyphenol; materials of the formula

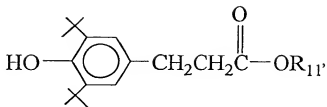


where X is zero to 5, R<sub>8</sub> and R<sub>9</sub> are the same or different and are C<sub>1</sub>-C<sub>20</sub> hydrocarbyl which may contain oxygen or sulfur or be substituted with oxygen or sulfur containing groups; and materials of the formula



where y is 1 to 4 and R<sub>10</sub> is a C<sub>1</sub> to C<sub>20</sub> hydrocarbyl which may contain oxygen sulfur or nitrogen or be substituted with oxygen, sulfur or nitrogen containing groups such as 2,6 di tert butyl α dimethylamino P-cresol,

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IV

wherein it is believed  $\text{R}_{11}$  is  $\text{C}_8\text{C}_{17}$  (CAS # 125643-61-0), and mixtures of such phenolic type antioxidants.

Preferably the phenolic anti-oxidant contains an ester group, such as in formula IV above.

Phenolic type anti oxidants are typically used at a concentration of from about 0.01 to 2.0 wt%, preferably about 0.1 to 1.0 wt%, most preferably about 0.3 to 0.5 wt%, based on active ingredient.

In order to prevent or at least minimize the formation of crystals in lubricating oils based on base stock having less than 99% saturates preferably less than 98 wt% saturates and containing a mixture of sulfur-organo phosphorus anti-wear/extreme pressure additive and phenolic anti-oxidant, wherein the sulfur phosphorus containing anti-wear/extreme pressure agent interests with the hindered phenol to produce crystals a minor, crystal preventing effective amount of a high molecular weight carboxylic acid, anhydride or mixture thereof is added to the lubricating oil formulation.

The carboxylic acid or anhydride can be any high molecular weight acid such as di- or polycarboxylic acid, anhydride or mixture thereof of molecular weight of about 300-5000. Such acids, anhydrides or mixtures thereof include polyhydrocarbylene substituted di- or polycarboxylic acids or anhydrides wherein the poly hydrocarbylene group has a molecular weight in the range 300 to 5000, preferably 750 to 2000, most preferably 900 to 1000 (e.g.,

- 5 polyisobutylene) and wherein the carboxylic group is, e.g., succinic or maleic acid, anhydride or mixture thereof.

Poly hydrocarbylenes are homopolymer or interpolymers of polymerizable olefin group containing monomers having from 2 to 16 carbons.

- 10 Interpolymers are those made using two or more different olefinic groups containing monomer including monomer such as styrenes. Poly hydrocarbylene homo and interpolymers are well known in the literature and to those skilled in the art and need not be further described herein.

- 15 Preferably the carboxylic acid or anhydride or mixture thereof used is polyalkylene succinic or maleic acid, anhydride, or mixtures thereof, most preferably polyisobutylene (PIB) succinic acid, anhydride or mixtures thereof wherein the PIB group has a molecular weight of about 900 to 1000.

- 20 Such high molecular weight carboxylic acids, anhydrides are employed in an amount in the range of about 0.0026 to 0.8 wt%, preferably about .08 to 0.4 wt%, most preferably about 0.12 to 0.24 wt%, based on active ingredients.

- 25 In general, at least 0.0013 wt% of high molecule weight carboxylic acid, anhydride or mixture thereof is used for each 1 ppm phosphorous from the sulfur-organo phosphorus anti-wear/extreme pressure agent.

### EXAMPLES

- 30 Example 1

This example (Table 1) is presented to show that, in a base stock having a saturates content of less than 99 wt%, the combination of a sulfur-

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- 5 phosphorous anti-wear/extreme pressure agent with a hindered phenol results in crystal formation while the combination of a sulfur free phosphate extreme pressure agent and hindered phenol does not result in crystal formation.

TABLE 1

			Crystals at 3 months
Base oil (1)	+ .55 wt% sulfur-phosphorus extreme pressure agent (2)	+ 0.4 wt% hindered phenol (3)	yes
Base oil (1)	+ .4 wt% hindered phenol	+ .55 wt% sulfur free phosphate EP agent (4)	no

10

- (1) solvent refined base oil, about 88% saturates 150 SN oil  
 (2) sulfur phosphorus extreme pressure agent CAS #83547-95-9 which is 60% sulfur-phosphorus component active ingredient (also contained C<sub>4</sub>-C<sub>8</sub> diphenyl amine as balance of additive)  
 15 (3) 100% active ingredient, CAS # 125643-61-0  
 (4) 100% active ingredient, isopropylated triaryl phosphate

The resulting lubricant had a phosphorus content of 120ppm by weight, measured according to standard test ASTM D5185-97, attributable to the sulphur-phosphorus extreme pressure agent (which was the sole phosphorus-containing component contained in the lubricant formulation)

20

Example 2

- This example (Table 2) is presented to show that crystal formation is  
 25 eliminated in formulations normally exhibiting crystal formation by the addition of high molecular weight anhydride but that crystal formation is not eliminated by the addition of high molecular weight anhydride-poly amine dispersant, or by the addition of esters. All formulations tested in this example further contained typical pour point depressants, anti-rust agent and an amino para cresol  
 30 antioxidant.

TABLE 2

Base oil (1)	+ .55 wt% sulfur-phosphorus EP agent (2)	+ 0.4 wt% hindered phenol (3)	+	Crystals at 3 months	
					yes
(“)	(“)	(“)	+	PIBSA + PAM (4)	yes
(“)	(“)	(“)	+	Esters (5)	yes
(“)	(“)	(“)	+	PIBSA (6)	yes
(“)	(“)	(“)	+	PIBSA (7)	no

(1) Base oil, a 50/50 mixture of 150 N (88% saturates) and 400 N (about 78% saturates).

(2) See Table 1.

(3) See Table 1.

(4) PIBSA-PAM was tested at concentration of from 0.05 to .4 wt% and at all concentrations used crystals formed within the three month time period of the test.

(5) Esters tested were di iso nonyl phthalate at 0.05 to 4 wt%, di iso-tridecyl adipate at .1 to .5 wt%, C<sub>6</sub> and C<sub>13</sub> phthalate at .5 wt%. None were effective at eliminating crystal formation during the three month time period of the test.

(6) PIBSA is polyisobutylene succinic anhydride, having a polyisobutylene molecular weight of 950. When used at .04 wt% and .08 wt% active ingredient level, it did not eliminate crystal formation.

(7) PIBSA (of note 6) at .16 wt% and .32 wt% active ingredient level eliminated crystal formation.

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Example 3

This example (Table 3) is presented to show the effect of base stock saturation on the suppression of crystal formation when using PIBSA in  
10 combination with sulfur phosphorus extreme pressure agent and hindered phenol.



TABLE 3

Base oil (1)	+	0.55 wt% sulfur phosphorus extreme pressure agent (2)	+	0.4 wt% hindered phenol (3)	+	0.16 wt% PIBSA (4)	Crystals at 3 months
Base oil (5)		(“)		(“)		(“)	no
Base oil (6)		(“)		(“)		(“)	no
Base oil (7)		(“)		(“)		(“)	no
Base oil (8)		(“)		(“)		(“)	cloudy
Base oil (9)		(“)		(“)		(“)	cloudy
Base oil (10)		(“)		(“)		(“)	cloudy
Base oil (10)		(“)		(“)		PIBSA @ .8% AI	yes

(1) See Table 1.

(2) See Table 1.

(3) See Table 1.

(4) PIBSA is polyisobutylene succinic anhydride, polyisobutylene molecular weight 950.

(5) 150 N, about 80% saturates.

(6) 150N FDA C grade white oil about 80% saturate (by clay-gel analysis - ASTM D 2007).

(7) Hydrocracked 90 N, about 92% saturates.

(8) 150 N FDA A grade white oil, 100% saturates

(9) Hydrocracked 150 N, about 99.9% saturates.

(10) PAO-6, 100% saturates.

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From this it is seen that in base oils having less than 99% saturates and containing mixtures of sulfur-phosphorus extreme pressure agent and hindered phenol, which are prone to crystal formation, crystal formation is suppressed on adding PIBSA where as in base oils of essentially 100% saturates  
10 content even addition of PIBSA failed to prevent crystal formation and even increasing PIBSA concentrate to 0.8 wt% (active ingredient) did not prevent crystal formation.

5    CLAIMS :

1. A lubricating oil of reduced crystal formation potential attributable to the interaction of sulfur phosphorus containing anti-wear/extreme pressure agents and hindered phenolic antioxidants comprising a major amount of a base oil of lubricating viscosity and having less than about 99 wt% saturates content, and a minor amount of additive comprising a sulfur-phosphorus containing anti-wear/extreme pressure additive, a hindered phenol antioxidant and a high molecular weight di- or poly- carboxylic acid, anhydride or mixture thereof provided at least 0.0013 wt% high molecular weight carboxylic acid, anhydride or mixture thereof is present for each 1 ppm phosphorus attributable to the sulfur phosphorus containing anti-wear/extreme pressure agent.

2. The lubricating oil of claim 1 wherein the sulfur-phosphorus anti-wear/extreme pressure agent is in an amount sufficient to provide about 2 ppm to 320 ppm phosphorus, the hindered phenol antioxidant is at a concentration of from about 0.01 to 2.0 wt% based on active ingredient and the high molecular weight di- or poly-carboxylic acid is at a concentration of in the range of about 0.0026 to 0.8 wt% based on active ingredient.

3. The lubricating oil of claim 1 or 2 wherein the sulfur-phosphorus containing anti-wear/extreme pressure agent is in an amount sufficient to provide from 40 ppm to 200 ppm phosphorus.

4. The lubricating oil of claim 1 or 2 wherein the sulfur-phosphorus containing anti-wear/extreme pressure agent is in an amount sufficient to provide from 80 ppm to 130 ppm phosphorus.

5           5. The lubricating oil of any preceding claim wherein the hindered phenol is at a concentration of about 0.1 to 1.0 wt% based on active ingredient.

6. The lubricating oil of claim 2, 3 or 4 wherein the hindered phenol is at a concentration of about 0.3 to 0.5 wt% based on active ingredient.

10           7. The lubricating oil of claim 2, 3 or 4 wherein the high molecular weight di- or poly-carboxylic acid, anhydride or mixture thereof is at a concentration of about 0.08 to 0.4 wt% based on active ingredient.

15           8. The lubricating oil of any preceding claim wherein the high molecular weight di- or poly-carboxylic acid anhydride or mixture thereof is at a concentration of about 0.12 to 0.24 wt% based on active ingredient.

20           9. The lubricating oil of any preceding claim wherein the high molecular weight di- or poly-carboxylic acid, anhydride mixture thereof is a polyhydrocarbylene substituted di- or poly-carboxylic acid, anhydride or mixture thereof wherein the polyhydrocarbylene group has a molecular weight in the range 300 to 5,000.

25           10. A method for reducing crystal formation in lubricating oil containing a mixture of sulfur phosphorus anti-wear/extreme pressure agent and hindered phenols antioxidant wherein the sulfur-phosphorus anti-wear/extreme pressure agent interacts with the phenolic antioxidant to produce crystals, such method comprising adding to a major amount of a base oil of lubricating  
30           viscosity having a saturates content of less than 99 wt%, a minor amount of additives comprising a sulfur-phosphorus containing anti-wear/extreme pressure agent a hindered phenol antioxidant and a high molecular weigh di- or poly-carboxylic acid, anhydride or mixture thereof provided at least 0.0013 wt% of

- 18 -

- 5 the high molecular weight di- or poly-carboxylic acid, anhydride or mixture thereof is used for each 1 ppm phosphorus attributable to the sulfur-phosphorus containing anti-wear/extreme pressure agent.

5

ABSTRACT

10/069321

STABILIZED LUBRICATING FORMULATION AND METHOD

10

Lubricating oil formulations comprising base oil, sulfur-phosphorous anti-wear/extreme pressure agents and hindered phenol antioxidants which anti-wear/extreme-pressure agents and hindered phenolic antioxidants are prone to crystal formation wherein the base oil is characterized as having a saturates content of less than 99% are stabilized against crystal formation by the addition of a minor amount of a high molecular weight di- or polycarboxylic acid anhydride, or mixture thereof.

US

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Annex US.III, page 1

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER

**P1999S004**

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**" CRYSTAL FORMATION INHIBITION IN LUBRICATING COMPOSITIONS "**

the specification of which (check only one item below):

☐ is attached hereto.☐ was filed as United States application

Serial No.

on

and was amended

on \_\_\_\_\_ (if applicable).

☒ was filed as PCT international applicationNumber **PCT/EP00/07910**on **11 August 2000**

And was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

COUNTRY (if PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119	
GB	9919490.4	17 August 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

US

PCT Applicant's Guide - Volume II - National Chapter - US Annex US.III, page 2

**Combined Declaration For Patent Application and Power of Attorney (Continued)**  
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER

P1999S004

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.		
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

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1	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201	SIGNATURE OF INVENTOR 202	SIGNATURE OF INVENTOR 203	SIGNATURE OF INVENTOR 204
DATE	DATE	DATE	DATE